International Patent Publication No. WO 96/06887 A1

VDF copolymerized with fluorinated surfactant

1

INTERNATIONAL PATENT OFFICE

PATENT JOURNAL

INTERNATIONAL PATENT PUBLICATION NO. WO 96/06887 A1

Int. Cl.[6]:

C 08 L 27/16
C 09 D 127/16
C 08 L 51/06
C 09 D 151/06
C 08 F 214/22
216/14

Application No.: PCT/JP95/01679

Application Date: August 23, 1995

Publication Date: March 7, 1996

Priority:
   No: Hei 6[1994]-207359
   Date: August 31, 1994
   Country: Japan

Designated Contracting State: CN, KR, US, European Patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

AQUEOUS DISPERSION OF VINYLIDENE FLUORIDE
COPOLYMER, AQUEOUS DISPERSION OF VINYLIDENE
FLUORIDE SEED POLYMER, AND THEIR MANUFACTURING METHODS

Inventors and;
Inventors/Applicants (USA only):

Nobuhiko Tsuda
c/o Yodogawa Works,
Daikin Industries, Ltd.
1-1 Nichiichiya,
Settsu-shi, Osaka-fu

Iwakiri Ryuzi
c/o Yodogawa Works,
Daikin Industries, Ltd.
1-1 Nichiichiya,
Settsu-shi, Osaka-fu

Yasushi Yonei
c/o Yodogawa Works,
Daikin Industries, Ltd.
1-1 Nichiichiya,
Settsu-shi, Osaka-fu

Katsuhiko Imoto
c/o Yodogawa Works,
Daikin Industries, Ltd.
1-1 Nichiichiya,
Settsu-shi, Osaka-fu

Yoshiki Shimizu
c/o Yodogawa Works,
Daikin Industries, Ltd.
1-1 Nichiichiya,
Settsu-shi, Osaka-fu

Takayuki Araki
c/o Yodogawa Works,
Daikin Industries, Ltd.
1-1 Nichiichiya,
Settsu-shi, Osaka-fu

                                        Masahiro Kondo
                                        c/o Yodogawa Works,
                                        Daikin Industries, Ltd.
                                        1-1 Nichiichiya,
                                        Settsu-shi, Osaka-fu

Applicant   Daikin Industries, Ltd.
(for all contracting   2-4-12 Nakazakinishi,
states except USA):   Kita-ku, Osaka-shi,
                                        Osaka-fu

Agent: Sohta Asahina, patent
                                        attorney

[There are no amendments to this patent.]

An aqueous dispersion of a vinylidene fluoride (VdF) copolymer which is produced by the emulsion polymerization of VdF monomer and a reactive emulsifier, wherein the average particle diameter of the copolymer is as small as 200 nm or less, while the solid concentration is as high as 30-60 wt.%, and which is excellent in sedimentation stability; and an aqueous dispersion of a VdF seed polymer which is produced by the seed polymerization of an ethylenically unsaturated monomer in the presence of the particles obtained by the emulsion polymerization of VdF monomer and a reactive emulsifier, wherein the average particle diameter of the seed polymer is as small as 250 nm or less, while the solid concentration is as high as 30-60 wt.%, and which is excellent in sedimentation stability.

FOR INFORMATION ONLY

Codes for the identification of PCT contract states
on the cover sheets of the documents that publish the
international applications in accordance with the PCT.

AL	Albania	IR	Iran	NZ	New Zealand
AM	Armenia	IS	Iceland	PL	Poland
AT	Austria	IT	Italy	PT	Portugal
AU	Australia	JP	Japan	RO	Romania
AZ	Azerbaijan	KE	Kenya	RU	Russian
BA	Bosnia-Herzegovina	KG	Kirgizstan		Federation
BB	Barbados	KP	Korean Democratic	SD	Sudan
BE	Belgium		People's Republic	SE	Sweden
BF	Burkina Faso	KR	South Korea,	SG	Singapore
BG	Bulgaria		Republic of Korea	SI	Slovenia
BJ	Benin	KZ	Kazakhstan	SK	Slovak Republic
BR	Brazil	LI	Liechtenstein		or Slovakia,
BY	Belarus	LK	Sri Lanka		follow original
CA	Canada	LR	Liberia	SN	Senegal
CF	Central African	LS	Lesotho	SZ	Swaziland
	Republic	LT	Lithuania	TD	Chad
CG	Congo	LU	Luxembourg	TG	Togo
CH	Switzerland	LV	Latvia	TJ	Tadjikstan
CI	Ivory Coast	MC	Monaco	TM	Turkmenistan
CM	Cameroon	MD	Republic of	TR	Turkey
CN	China		Moldavia	TT	Trinidad and
CZ	Czech Republic	MG	Madagascar		Tobago
DE	Germany	MK	Macedonia (formerly	UA	Ukraine
DK	Denmark		part of	UG	Uganda
EE	Estonia		Yugoslavian	US	United States
ES	Spain		Federation Socialist		of America
FI	Finland		Republic)	UZ	Uzbekistan
FR	France	ML	Mali	VN	Vietnam
GA	Gabon	MN	Mongolia		
GB	United Kingdom	MR	Mauritania		
GE	Georgia	MW	Malawi		
GN	Guinea	MX	Mexico		
GR	Greece	NE	Niger		
HU	Hungary	NL	Netherlands		
IE	Ireland	NO	Norway		

Technical field

The present invention pertains to an aqueous dispersion of a vinylidene fluoride copolymer, an aqueous dispersion of a vinylidene fluoride seed polymer, and their manufacturing methods. The above-mentioned aqueous dispersion of the vinylidene fluoride copolymer and the above-mentioned aqueous dispersion of the vinylidene fluoride seed copolymer can be appropriately used in aqueous coating paints, etc.

Prior art

As a conventional paint for various kinds of buildings, a fluorinated paint with excellent water resistance and weather resistance is used. However, as the above-mentioned fluorinated paint, many types of organic solvent may be used, and an aqueous type is required in terms of safety and environmental protection. Many proposals have been made for the use and manufacturing method of a base of an aqueous fluorinated paint as an aqueous dispersion of a fluorine polyme.

For example, in Japanese Kokoku Patent No. Sho 61[1986]-33848, a method for manufacturing an aqueous dispersion of a vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene elastomer containing fluorine with a particle diameter of 0.02 μm in the presence of a fluorinated surfactant having a polymerizable double bond represented by $CF_2=CF-O-(-CF_2-)_n-COOM$ (where n represents an integer of 1-7; M represents an amine or alkali metal) is described. However, although an aqueous dispersion with a small particle diameter is obtained, since the concentration of

said elastomer in said dispersion is 25 wt% or less, the viscosity-enhancing effect by a viscosity adjustor is insufficient for an aqueous paint. Furthermore, in increasing the solid fraction concentration, there is no description as to the stability of the dispersion, and there is also no description as an aqueous paint.

Also, in Japanese Kokoku Patent No. Hei 4[1992]-55441, a method for the emulsion polymerization of an ethylenically unsaturated monomer in the presence of fluorinated copolymer particles in an aqueous medium is described, and in Japanese Kokai Patent Application No. Hei 3[1991]-7784, a method for the emulsion polymerization of an ethylenically unsaturated monomer in the presence of vinylidene fluoride copolymer particles in an aqueous medium is described. However, in these methods, although it is described that an acrylic monomer undergoes seed polymerization, there is no description as to the control of the particle diameter of the seed particle used in the seed polymerization and there is no description of the use of the seed particle in a reactive emulsifier in the seed polymerization. Furthermore, if a seed particle of 50 nm or less is used, since the viscosity of the obtained aqueous dispersion is increased, an aqueous dispersion with a high solid fraction concentration cannot be obtained, and solidification and precipitation are generated when it is used under high shear.

Also, in Japanese Kokoku Patent No. Sho 50[1975]-4396, a method which copolymerizes acrylic acid during polymerization in an acrylic group emulsion and obtains a microemulsion with an average particle diameter of 50 nm or less by neutralizing the generated emulsion with ammonia is described. However, in the polymerization of a fluorinated olefin, in particular, a

vinylidene fluoride monomer, if a nonfluorinated carboxylic acid monomer such as acrylic acid is present, since said polymerization is markedly hindered, the polymerization of the fluorinated olefin in such a system does not occur.

Also, in Japanese Kokoku Patent No. Sho 49[1974]-17858, a method for copolymerizing a fluorinated vinyl compound having a -COOH group on the side chain to introduce a crosslinking group in a linear, saturated fluorinated elastic resin is described; however, there is no description as to the aqueous dispersion, particle diameter control of particles in said dispersion, and aqueous paint.

Also, in "High-Molecular Substance Thesis Collection," Vol. 36, No. 11, pp.729-737 (1979), it is described that if a large amount of various kinds of surfactants is used in emulsion polymerization, the size of the polymer particles decreases and even if a mixture of an anionic surfactant and a nonionic surfactant is used in the polymerization of an acrylic monomer, an effect similar to that when using the anionic surfactant is obtained. If a large amount of said surfactant is used, when a film is formed as an emulsion paint, said surfactant is precipitated, or the water resistance of the film is lowered.

Also, in Japanese Kokai Patent Application Nos. Hei 5[1993]-79249, Hei 5[1993]-85575, and Hei 5[1993]-255222, it is presented that $CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_n-CF(CF_3)Y$, $CF_2=CF-O-(-CFX-)_n-Y$ (where n represents an integer and Y represents SO_3M or COOM (M represents an amine salt or alkali metal), X represents F or CF_3), etc., are copolymerized with tetrafluoroethylene and used as an ion exchange film. However, although examples such as solution polymerization are mentioned to obtain the ion exchange film, there is no example of emulsion

polymerization in an aqueous medium, and there is also no description as to an aqueous paint.

The objective of the present invention is to provide an aqueous dispersion of a vinylidene fluoride copolymer with an average particle diameter of the copolymer as small as 200 nm or lower, a solid fraction concentration of the aqueous dispersion as high as 30-60 wt%, and excellent sedimentation stability, an aqueous dispersion of a vinylidene fluoride seed copolymer with an average particle diameter of the seed copolymer as small as 250 nm or lower and a solid fraction concentration of the aqueous dispersion as high as 30-60 wt%, and their manufacturing methods, and to give water resistance, weather resistance, chemical resistance, and high-gloss film formability to an aqueous paint manufactured using each dispersion.
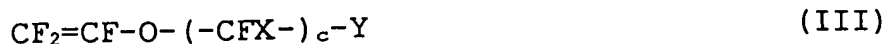
Presentation of the invention

The present invention pertains to an aqueous dispersion of a vinylidene fluoride copolymer of a vinylidene fluoride monomer characterized in that at least one reactive emulsifier selected from a group comprised of general formula (I):
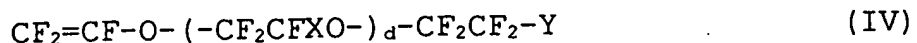
$$CF_2=CF-(-CF_2-)_a-Y \qquad (I)$$

(where a represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (II):
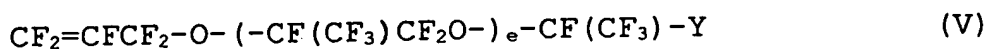
$$CF_2=CF-(-CF_2CFX-)_b-Y \qquad (II)$$

(where X represents F or CF_3, b represents an integer of 1-5, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (III):
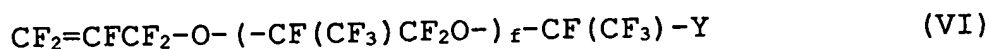
$$CF_2=CF-O-(-CFX-)_c-Y \qquad (III)$$

(where X represents F or CF₃, c represents an integer of 1–10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal), general formula (IV):

$$CF_2=CF-O-(-CF_2CFXO-)_d-CF_2CF_2-Y \qquad (IV)$$

(where X represents F or CF₃, d represents an integer of 1–10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (V):
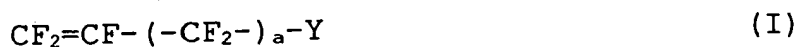
$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_e-CF(CF_3)-Y \qquad (V)$$

(where e represents an integer of 1–10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), and general formula (VI):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_f-CF(CF_3)-Y \qquad (VI)$$

(where f represents an integer of 1–10, Y represents SO_3M or COOM (M represents H, NH_4, or alkali metal)), the solid fraction concentration is 30–60 wt% and the average particle diameter of said copolymer is 200 nm or less.

Also, the present invention pertains to a method for manufacturing the aqueous dispersion of the vinylidene fluoride copolymer by the emulsion polymerization of a vinylidene fluoride monomer and a reactive emulsifier; as said reactive emulsifier, at least one kind is selected from a group comprised of general formula (I):
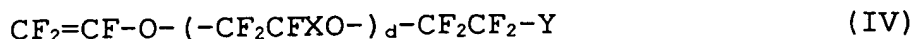
$$CF_2=CF-(-CF_2-)_a-Y \qquad (I)$$

(where a represents an integer of 1–10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (II):
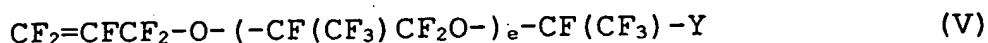
$$CF_2=CF-(-CF_2CFX-)_b-Y \qquad (II)$$

(where X represents F or CF₃, b represents an integer of 1–5, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (III):

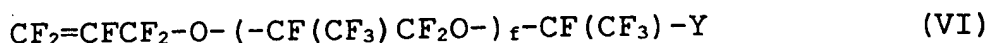$$CF_2=CF-O-(-CFX-)_c-Y \qquad (III)$$

(where X represents F or CF_3, c represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (IV):

$$CF_2=CF-O-(-CF_2CFXO-)_d-CF_2CF_2-Y \qquad (IV)$$

(where X represents F or CF_3, b represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (V):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_e-CF(CF_3)-Y \qquad (V)$$

(where e represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), and general formula (VI):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_f-CF(CF_3)-Y \qquad (VI)$$

(where f represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)) is used at 0.00001-10 wt%; the solid fraction concentration is set to 30-60 wt%; the average particle diameter of said copolymer is set to 200 nm or less.

Furthermore, the present invention pertains to an aqueous dispersion of a vinylidene fluoride seed polymer obtained by the emulsion polymerization of an ethylenically unsaturated monomer in the presence of vinylidene fluoride copolymer particles, said vinylidene fluoride copolymer is a copolymer of a vinylidene fluoride monomer and at least one reactive emulsifier selected from a group comprised of general formula (I):
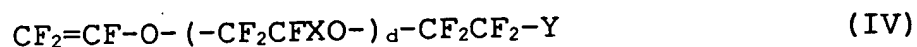
$$CF_2=CF-(-CF_2-)_a-Y \qquad (I)$$

(where a represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (II):

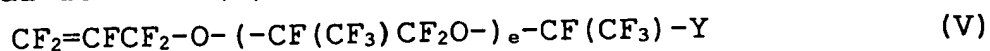$$CF_2=CF-(-CF_2CFX-)_b-Y \qquad (II)$$

(where X represents F or CF_3, b represents an integer of 1-5, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (III):

$$CF_2=CF-O-(-CFX-)_c-Y \qquad (III)$$

(where X represents F or CF_3, c represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (IV):

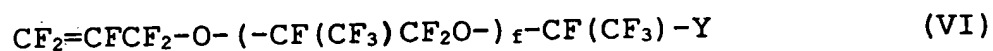$$CF_2=CF-O-(-CF_2CFXO-)_d-CF_2CF_2-Y \qquad (IV)$$

(where X represents F or CF_3, d represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (V):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_e-CF(CF_3)-Y \qquad (V)$$

(where e represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), and general formula (VI):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_f-CF(CF_3)-Y \qquad (VI)$$

(where f represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)); the solid fraction concentration of the aqueous dispersion of said seed polymer is 30-60 wt%; the average particle diameter of said seed copolymer is 250 nm or less.

Furthermore, the present invention pertains to a method for manufacturing the aqueous dispersion of the vinylidene fluoride seed polymer by the emulsion polymerization of an ethylenically unsaturated monomer in the presence of vinylidene fluoride copolymer particles, said vinylidene fluoride copolymer is manufactured by the emulsion polymerization of a vinylidene fluoride monomer and water and 0.00001-10 wt% at least one reactive emulsifier selected from a group comprised of general formula (I):
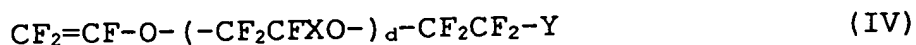
$$CF_2=CF-(-CF_2-)_a-Y \qquad (I)$$

(where a represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (II):
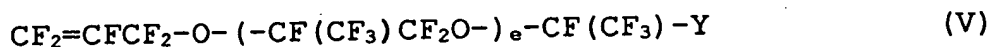
$$CF_2=CF-(-CF_2CFX-)_b-Y \qquad (II)$$

(where X represents F or CF_3, b represents an integer of 1-5, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (III):

$$CF_2=CF-O-(-CFX-)_c-Y \qquad (III)$$

(where X represents F or CF_3, c represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (IV):

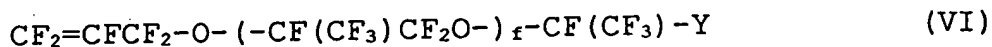$$CF_2=CF-O-(-CF_2CFXO-)_d-CF_2CF_2-Y \qquad (IV)$$

(where X represents F or CF_3, d represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (V):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_e-CF(CF_3)-Y \qquad (V)$$

(where e represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), and general formula (VI):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_f-CF(CF_3)-Y \qquad (VI)$$

(where f represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)); the solid fraction concentration of the aqueous dispersion of said seed polymer is set to 30-60 wt%; the average particle diameter of said seed copolymer is set to 250 nm or less.

Best application mode of the invention

The aqueous dispersion of the vinylidene fluoride copolymer in the present invention is an aqueous dispersion of a VdF

copolymer of a vinylidene fluoride (VdF) monomer and a reactive emulsifier.

The above-mentioned reactive emulsifier is a fluorinated compound having a polymerizable double bond and a hydrophilic group in the molecule and is a compound represented by at least one kind selected from the above-mentioned group comprised of general formula (I):
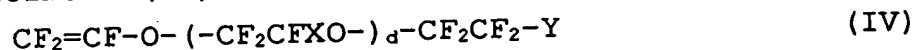
$$CF_2=CF-(-CF_2-)_a-Y \qquad (I)$$

(where a represents an integer of 1-10, Y represents SO_3M or $COOM$ (M represents H, NH_4, or an alkali metal)), general formula (II):

$$CF_2=CF-(-CF_2CFX-)_b-Y \qquad (II)$$

(where X represents F or CF_3, b represents an integer of 1-5, Y represents SO_3M or $COOM$ (M represents H, NH_4, or an alkali metal)), general formula (III):

$$CF_2=CF-O-(-CFX-)_c-Y \qquad (III)$$

(where X represents F or CF_3, c represents an integer of 1-10, Y represents SO_3M or $COOM$ (M represents H, NH_4, or an alkali metal)), general formula (IV):

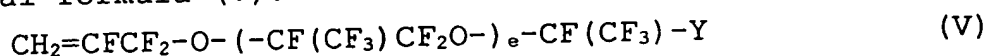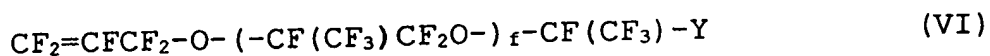$$CF_2=CF-O-(-CF_2CFXO-)_d-CF_2CF_2-Y \qquad (IV)$$

(where X represents F or CF_3, d represents an integer of 1-10, Y represents SO_3M or $COOM$ (M represents H, NH_4, or an alkali metal)), general formula (V):

$$CH_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_e-CF(CF_3)-Y \qquad (V)$$

(where e represents an integer of 1-10, Y represents SO_3M or $COOM$ (M represents H, NH_4, or an alkali metal)), and general formula (VI):

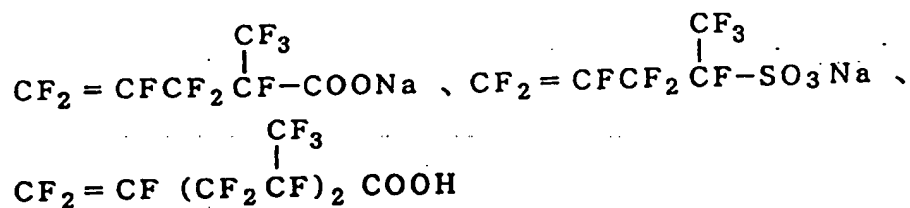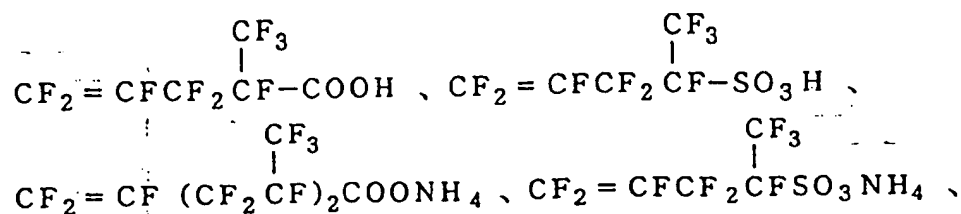$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_f-CF(CF_3)-Y \qquad (VI)$$

(where f represents an integer of 1-10, Y represents SO_3M or $COOM$ (M represents H, NH_4, or an alkali metal)).

In the above-mentioned general formula (I), a is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.
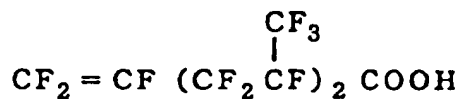
As detailed examples of the compound represented by the above-mentioned general formula (I), for example, $CF_2=CF-CF_2-COONH_4$, $CF_2=CF-CF_2-COOH$, $CF_2=CF-CF_2CF_2COOH$, $CF_2=CF-CF_2-COONa$, $CF_2=CF-CF_2-SO_3NH_4$, $CF_2=CF-CF_2-SO_3H$, $CF_2=CF-CF_2CF_2SO_3H$, $CF_2=CF-CF_2CF_2SO_3Na$, etc., are mentioned, however $CF_2=CFCF_2COONH_4$ is preferable since an aqueous dispersion of the VdF copolymer with a high concentration and a small particle diameter is obtained.

In the above-mentioned general formula (II), X is preferably CF_3 in terms of stability of the compound, b is preferably an integer of 1-3 in terms of surface activity of the reactive emulsifier, Y is preferably COOM and SO_3M in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (II), for example,

$$CF_2 = CFCF_2 \overset{\overset{\displaystyle CF_3}{|}}{C}F-COOH \ \text{、} \ CF_2 = CFCF_2 \overset{\overset{\displaystyle CF_3}{|}}{C}F-SO_3H \ \text{、}$$

$$CF_2 = CF \ (CF_2 \overset{\overset{\displaystyle CF_3}{|}}{C}F)_2 COONH_4 \ \text{、} \ CF_2 = CFCF_2 \overset{\overset{\displaystyle CF_3}{|}}{C}FSO_3NH_4 \ \text{、}$$

$$CF_2 = CFCF_2 \overset{\overset{\displaystyle CF_3}{|}}{C}F-COONa \ \text{、} \ CF_2 = CFCF_2 \overset{\overset{\displaystyle CF_3}{|}}{C}F-SO_3Na \ \text{、}$$

$$CF_2 = CF \ (CF_2 \overset{\overset{\displaystyle CF_3}{|}}{C}F)_2 \ COOH$$

are mentioned, however

$$CF_2 = CF \ (CF_2 \overset{\overset{\displaystyle CF_3}{|}}{C}F)_2 \ COOH$$

is preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (III), X is preferably F and CF_3 in terms of stability and weather resistance of the compound, c is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM and SO_3M in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.
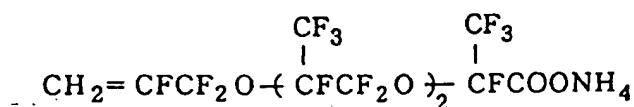
As detailed examples of the compound represented by the above-mentioned general formula (III), for example, $CF_2=CF-OCF_2CF_2CF_2COOH$, $CF_2=CF-OCF_2CF_2COONH_4$, $CF_2=CF-OCF_2COOH$, etc., are mentioned, however $CF_2=CF-OCF_2CF_2CF_2COOH$ is preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (IV), X is preferably F and CF_3 in terms of stability and weather resistance of the compound, d is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM and SO_3M in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.
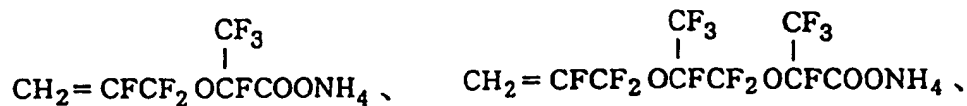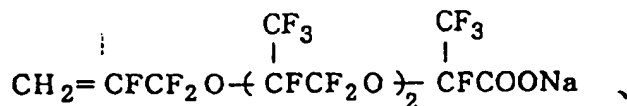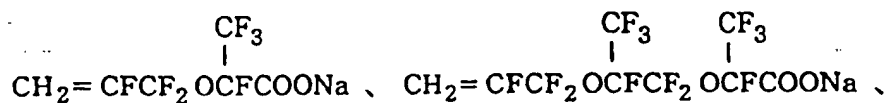
As detailed examples of the compound represented by the above-mentioned general formula (IV), for example, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COOH$, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COONH_4$, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2SO_3H$, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2SO_3NH_4$ or these ammonium salts, etc., are mentioned, however $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COOH$ and $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2SO_3H$ are preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (V), e is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM in terms of stability of the compound, and M is preferably Na and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (V), for example,

$$CH_2=CFCF_2OCFCOONa \quad , \quad CH_2=CFCF_2OCFCF_2OCFCOONa \quad ,$$
(with CF$_3$ branches)

$$CH_2=CFCF_2O \text{-}(CFCF_2O)_{\overline{2}} CFCOONa \quad ,$$

$$CH_2=CFCF_2OCFCOONH_4 \quad , \quad CH_2=CFCF_2OCFCF_2OCFCOONH_4 \quad ,$$

$$CH_2=CFCF_2O \text{-}(CFCF_2O)_{\overline{2}} CFCOONH_4$$

are mentioned, however $CH_2=CFCF_2OCF(CF_3)COONH_4$ and $CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COONH_4$ are preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (VI), f is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM in terms of stability of the compound, and M is preferably H and NH$_4$ in terms of water resistance of the film.
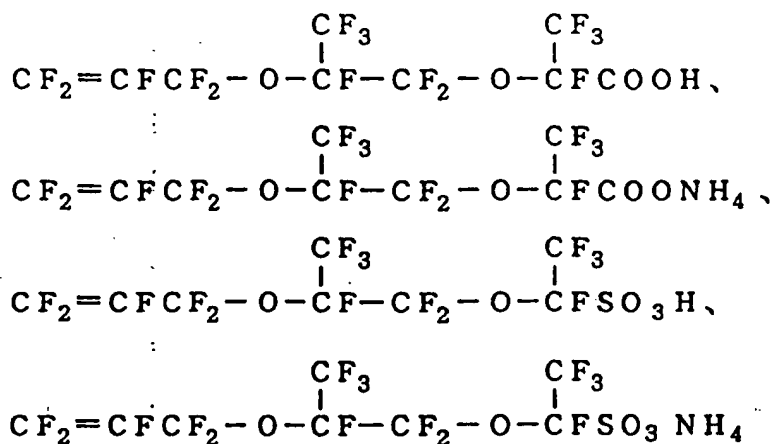
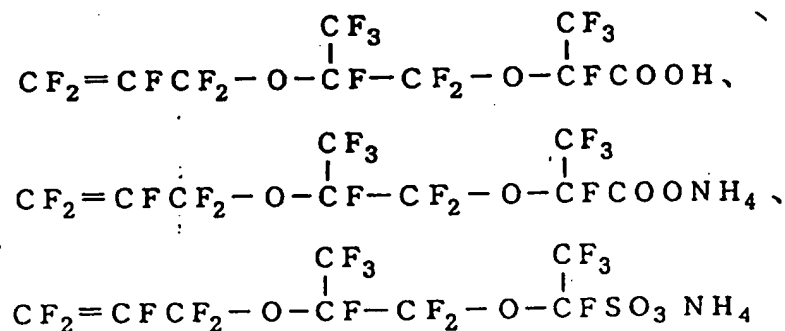As detailed examples of the compound represented by the above-mentioned general formula (VI), for example,

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FCOOH,$$

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FCOONH_4,$$

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FSO_3H,$$

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FSO_3NH_4$$

are mentioned, however

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FCOOH,$$

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FCOONH_4,$$

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FSO_3NH_4$$

is preferable since an aqueous dispersion of the VdF
group copolymer with a small particle diameter is obtained.

In the present invention, the above-mentioned VdF copolymer
may also be a copolymer containing another fluorinated monomer in

addition to the above-mentioned VdF monomer and the above-mentioned reactive emulsifier. As said other fluorinated monomer, for example, tetrafluoroethylene (TFE), trifluoroethylene (TrFE), chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), vinyl fluoride (VF), etc., are mentioned; however, TFE, HFP, and CTFE are preferable in terms of copolymerization reactivity of the VdF monomer.

As combinations for VdF, said other fluorinated monomer, and said reactive emulsifier in the above-mentioned VdF copolymer, for example, a combination of any of VdF/TFE, VdF/TFE/HFP, VdF/TFE/CTFE, VdF/TFE/TrFE, VdF/CTFE, VdF/HFP, VdF/VFE/HFP/CTFE, etc., and any of $CF_2=CFCF_2COONH_4$, $CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COONH_4$, $CH_2=CFCF_2OCF(CF_3)COONH_4$, etc., is mentioned; however, a combination of VdF/TFE/CTFE and $CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COONH_4$ is preferable in terms of film hardness in case it is used in coating.

The copolymerization ratio of the above-mentioned VdF and the above-mentioned other fluorinated monomer in the above-mentioned VdF copolymer is 60/40-95/5 wt%, preferably 70/30-95/5 wt%. If said VdF is less than 60 wt%, the compatibility with the acrylic polymer, which is a characteristic of the VdF polymer, tends to be lowered, and if it is more than 95 wt%, since the solubility of the seed particle into an acrylic ester and/or methacrylic acid ester is poor, the seed particle is not rapidly swollen to the monomer during seed polymerization. A cast film from the obtained emulsion has a poor transparency, and in preparing a film from the paint, gloss typically cannot be obtained.

The above-mentioned reactive emulsifier may be included at 0.001-0.1 mol% in relation to the combination of the above-mentioned monomer.

The average particle diameter of the above-mentioned VdF copolymer is 200 nm or less, preferably 10-200 nm, and more preferably 50-150 nm. If the above-mentioned average particle diameter is less than 10 nm, the shape of the VdF copolymer is difficult to form, and the film formability tends to decrease. If the diameter is more than 200 nm, the storage stability, mechanical stability, and chemical stability of the aqueous dispersion of the VdF copolymer tend to decrease.

The solid fraction concentration of the aqueous dispersion of the above-mentioned VdF copolymer is 30-60% (wt%, hereinafter, similarly applied), preferably 35-55%, and more preferably 35-50%. If the above-mentioned concentration is less than 30%, viscosity adjustment is difficult in forming a paint, and drying of the film tends to slow. If the concentration is more than 60%, the stability of the dispersion system tends to decrease.

In the aqueous dispersion of the VdF copolymer in the present invention, well-known fluorinated surfactants may also be included.

The above-mentioned well-known fluorinated surfactant is a mixture of one kind or two kinds or more of compounds, which include fluorine atoms in the structure and have surface activity. For example, the acid represented by $X(CF_2)_nCOOH$ (X represents F or H, and n represents an integer of 6-20) and its alkali metal salt, ammonium salt, amine salt, or quaternary ammonium salt, the acid represented by $Y(CH_2CF_2)_mCOOH$ (Y represents F or C, and l and m represent an integer of 6-13) and its alkali metal salt, ammonium salt, amine salt, or quaternary

ammonium salt, etc., are mentioned; however, the ammonium salt of perfluorooctanoic acid and the ammonium salt of perfluorononanoic acid are preferable in terms of weather resistance and water resistance.

The amount of said fluorinated surfactant used is 1.0% or less, preferably 0.5% or less, and more preferably 0.2% or less in relation to water. If the amount of said fluorinated surfactant used is more than 1.0%, when a film is formed from the aqueous dispersion, said fluorinated surfactant is precipitated in the film or the water absorption rate is increased, so that the surfactant tends to whiten, which is not preferable.

In the aqueous dispersion of the VdF copolymer in the present invention, a hydrophilic organic solvent can also be added.

The aqueous dispersion of the VdF copolymer of the present invention can form an aqueous paint by mixing with various kinds of additives. As the above-mentioned additives, for example, additives which are generally used in an aqueous paint, such as pigments, viscosity enhancers, dispersants, foaming agents, antifreezes, and film formation aids are mixed, so that a paint for building facades and civil structures can be formed.

Also, the present invention is a manufacturing method for obtaining the aqueous dispersion of the VdF copolymer through the emulsion polymerization of the VdF monomer and the reactive emulsifier.

The above-mentioned reactive emulsifier is a fluorinated compound having a polymerizable double bond and a hydrophilic group in the molecule and is a compound represented by at least one kind selected from the above-mentioned group comprised of general formula (I):
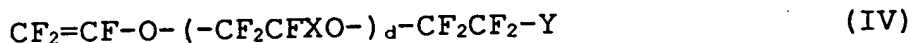
$$CF_2=CF-(-CF_2-)_a-Y \qquad (I)$$

(where a represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (II):

$$CF_2=CF-(-CF_2CFX-)_b-Y \qquad (II)$$

(where X represents F or CF_3, b represents an integer of 1-5, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (III):

$$CF_2=CF-O-(-CFX-)_c-Y \qquad (III)$$

(where X represents F or CF_3, c represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (IV):

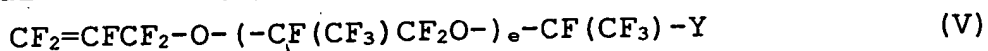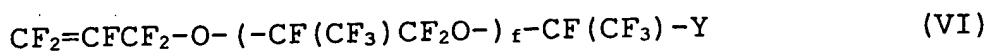$$CF_2=CF-O-(-CF_2CFXO-)_d-CF_2CF_2-Y \qquad (IV)$$

(where X represents F or CF_3, d represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (V):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_e-CF(CF_3)-Y \qquad (V)$$

(where e represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), and general formula (VI):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_f-CF(CF_3)-Y \qquad (VI)$$

(where f represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal).)
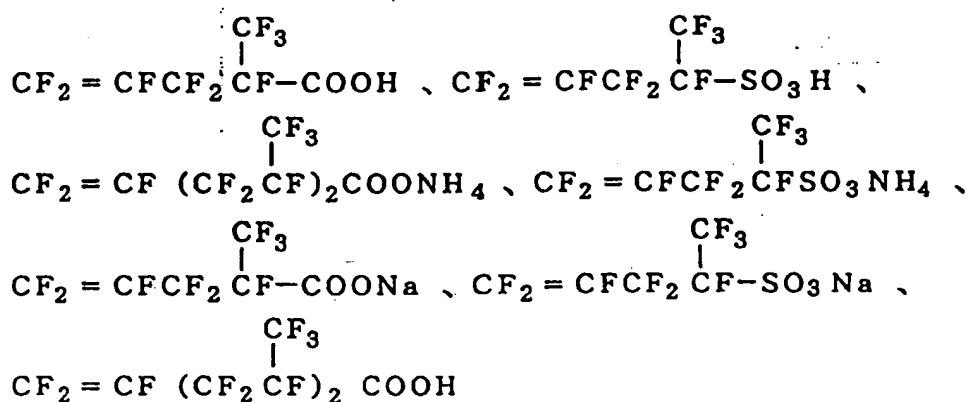
In the above-mentioned general formula (I), a is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (I), for example,

$CF_2=CF-CF_2-COONH_4$, $CF_2=CF-CF_2-COOH$, $CF_2=CF-CF_2CF_2COOH$, $CF_2=CF-CF_2-COONa$, $CF_2=CF-CF_2-SO_3NH_4$, $CF_2=CF-CF_2-SO_3H$, $CF_2=CF-CF_2CF_2SO_3H$, $CF_2=CF-CF_2CF_2SO_3Na$, etc., are mentioned; however, $CF_2=CFCF_2COONH_4$ is preferable since an aqueous dispersion of the VdF copolymer with a high concentration and a small particle diameter is obtained.

In the above-mentioned general formula (II), X is preferably CF_3 in terms of stability of the compound, b is preferably an integer of 1-3 in terms of surface activity of the reactive emulsifier, Y is preferably COOM and SO_3M in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.

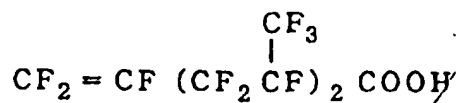As detailed examples of the compound represented by the above-mentioned general formula (II), for example,

$$CF_2 = CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{CF}-COOH \text{ , } CF_2 = CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{CF}-SO_3H \text{ ,}$$

$$CF_2 = CF(CF_2\overset{\overset{\displaystyle CF_3}{|}}{CF})_2COONH_4 \text{ , } CF_2 = CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{CF}SO_3NH_4 \text{ ,}$$

$$CF_2 = CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{CF}-COONa \text{ , } CF_2 = CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{CF}-SO_3Na \text{ ,}$$

$$CF_2 = CF(CF_2\overset{\overset{\displaystyle CF_3}{|}}{CF})_2 COOH$$

are mentioned; however,

$$CF_2 = CF \ (CF_2 \underset{\underset{CF_3}{|}}{CF})_2 \ COOH$$

is preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (III), X is preferably F and CF_3 in terms of stability and weather resistance of the compound, c is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM and SO_3M in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (III), for example, $CF_2=CF-OCF_2CF_2CF_2COOH$, $CF_2=CF-OCF_2CF_2COONH_4$, $CF_2=CF-OCF_2COOH$, etc., are mentioned; however, $CF_2=CF-OCF_2CF_2CF_2COOH$ is preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (IV), X is preferably F and CF_3 in terms of stability and weather resistance of the compound, d is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM and SO_3M in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (IV), for example, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COOH$, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COONH_4$, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2SO_3H$, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2SO_3NH_4$ or these ammonium salts, etc., are mentioned; however,

$CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COOH$ and $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2SO_3H$ are preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (V), e is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM in terms of stability of the compound, and M is preferably Na and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (V), for example,

$$CH_2=CFCF_2OCFCOONa \quad , \quad CH_2=CFCF_2OCFCF_2OCFCOONa \quad , $$

with the CF_3 substituents as shown,

$$CH_2=CFCF_2O-(CFCF_2O)_2-CFCOONa \quad , $$

$$CH_2=CFCF_2OCFCOONH_4 \quad , \quad CH_2=CFCF_2OCFCF_2OCFCOONH_4 \quad , $$

$$CH_2=CFCF_2O-(CFCF_2O)_2-CFCOONH_4$$

are mentioned; however, $CH_2=CFCF_2OCF(CF_3)COONH_4$ and $CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COONH_4$ are preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

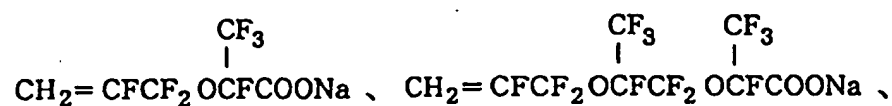In the above-mentioned general formula (VI), f is preferably an integer of 1-5 in terms of surface activity of the reactive

emulsifier, Y is preferably COOM in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.

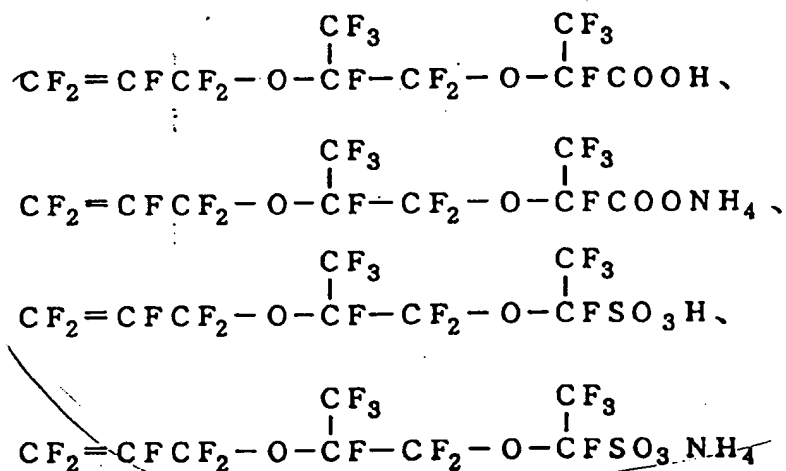As detailed examples of the compound represented by the above-mentioned general formula (VI), for example,

$$CF_2{=}CFCF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}F{-}CF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}FCOOH,$$

$$CF_2{=}CFCF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}F{-}CF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}FCOONH_4,$$

$$CF_2{=}CFCF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}F{-}CF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}FSO_3H,$$

$$CF_2{=}CFCF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}F{-}CF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}FSO_3 NH_4$$

are mentioned; however,

$$CF_2{=}CFCF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}F{-}CF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}FCOOH,$$

$$CF_2{=}CFCF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}F{-}CF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}FCOONH_4,$$

$$CF_2{=}CFCF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}F{-}CF_2{-}O{-}\underset{\underset{CF_3}{|}}{C}FSO_3 NH_4$$

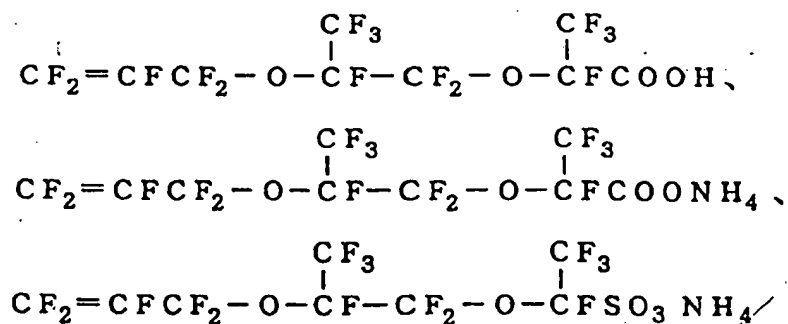is preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

When the above-mentioned VdF copolymer and the above-mentioned reactive emulsifier go through emulsion-polymerized, other fluorinated monomers can also be used in addition to VdF. For example, tetrafluoroethylene (TFE), trifluoroethylene (TrFE), chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), vinyl fluoride (VF), etc., are mentioned; however, TFE, HFP, and CTFE are preferable in terms of copolymerization reactivity of the VdF monomer.

In the above-mentioned emulsion polymerization, well-known fluorinated surfactants may also be included.

The above-mentioned well-known fluorinated surfactant is a mixture of one kind or two kinds or more of compounds which include fluorine atoms in the structure and have surface activity. For example, the acid represented by $X(CF_2)_nCOOH$ (X represents F or H, and n represents an integer of 6-20) and its alkali metal salt, ammonium salt, amine salt, or quaternary ammonium salt, the acid represented by $Y(CH_2CF_2)_mCOOH$ (Y represents F or C, and l and m represent an integer of 6-13) and its alkali metal salt, ammonium salt, amine salt, or quaternary ammonium salt, etc., are mentioned; however, the ammonium salt of perfluorooctanoic acid and the ammonium salt of perfluorononanoic acid are preferable in terms of weather resistance and water resistance.

The amount of said fluorinated surfactant used is 1.0% or less, preferably 0.5% or less, and more preferably 0.2% or less in relation to water. If the amount of said fluorinated surfactant used is more than 1.0%, when a film is formed from the aqueous dispersion, said fluorinated surfactant is precipitated

in the film or the water absorption rate is increased, so that the surfactant tends to whiten, which is not preferable.

In manufacturing the aqueous dispersion of the above-mentioned VdF copolymer, water is charged as a polymerization solvent into a reactor, and the above-mentioned reactive emulsifier is charged at 0.00001-10%, preferably 0.0001-1.0%, and more preferably 0.001-0.5% in relation to said polymerization solvent. Then, the dissolved air is removed by repeating nitrogen pressurization and degassing.

Here, if the amount of said reactive emulsifier charged is less than 0.00001%, large particles with insufficient sedimentation stability tend to form. If the amount is more than 10%, the shape of the particles is not spherical, and the film formability tends to decrease when drying the aqueous dispersion.

Next, the above-mentioned VdF monomer or a mixed monomer with another fluorinated monomer is supplied while pressurizing up to a pressure of 1.0-50 kgf/cm^2.

At that time, the mixture ratio of the above-mentioned other fluorinated monomer may be 0-30 wt%.

Next, as a polymerization initiator, for example, a persulfate such as ammonium persulfate, hydrogen peroxide, diisopropyl peroxydicarbonate, azobisisobutylonitrile, etc., is charged at 0.005-1.0%, preferably 0.01-0.5% in relation to water. If the amount of said polymerization initiator charged is less than 0.005%, the polymerization rate tends to decrease extremely. If the amount is more than 1.0%, the electrolyte concentration increases, and the particle diameter tends to increase.

Furthermore, the above-mentioned VdF monomer or the above-mentioned mixed monomer is continuously supplied so that the

pressure in the reactor can be constant in a range of
1.0-50 kgf/cm^2.

In the above-mentioned state, polymerization is carried out
for 5-100 h.

Then, the interior of the above-mentioned reactor returns to
normal temperature and normal pressure, and polymerization is
completed, so that the aqueous dispersion of the VdF copolymer is
obtained.

The average particle diameter of the VdF copolymer of the
aqueous dispersion of the VdF copolymer obtained by the above-
mentioned manufacturing method can be controlled to 200 nm or
less, and said average particle diameter can be controlled by the
amount of said reactive emulsifier charged.

Also, the solid fraction concentration of the aqueous
dispersion of the VdF copolymer obtained by the above-mentioned
manufacturing method can be controlled to 30-60%, and said
concentration can be controlled by blowing the VdF monomer or
mixed monomer when a prescribed amount of said VdF monomer or
said mixed monomer is supplied continuously to the reactor,
stirring is stopped, and the reaction is completed.

Furthermore, the aqueous dispersion of the VdF seed polymer
in the present invention is an aqueous dispersion of a VdF seed
polymer obtained by the emulsion polymerization of an
ethylenically unsaturated monomer in the presence of VdF
copolymer particles, and said VdF copolymer is a copolymer of a
VdF monomer and a reactive emulsifier.

The above-mentioned reactive emulsifier is a fluorinated
compound having a polymerizable double bond and a hydrophilic
group in the molecule and is a compound represented by at least

one kind selected from the above-mentioned group comprised of general formula (I):
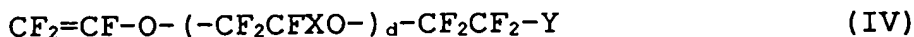
$$CF_2=CF-(-CF_2-)_a-Y \qquad (I)$$

(where a represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (II):

$$CF_2=CF-(-CF_2CFX-)_b-Y \qquad (II)$$

(where X represents F or CF_3, b represents an integer of 1-5, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (III):

$$CF_2=CF-O-(-CFX-)_c-Y \qquad (III)$$

(where X represents F or CF_3, c represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (IV):

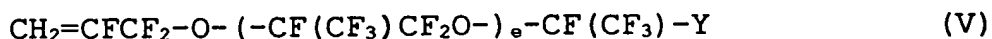$$CF_2=CF-O-(-CF_2CFXO-)_d-CF_2CF_2-Y \qquad (IV)$$

(where X represents F or CF_3, d represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (V):

$$CH_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_e-CF(CF_3)-Y \qquad (V)$$

(where e represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), and general formula (VI):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_f-CF(CF_3)-Y \qquad (VI)$$
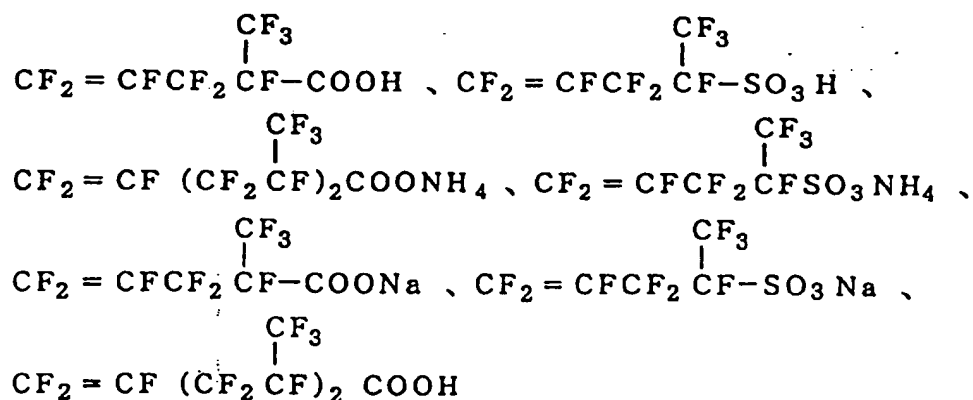
(where f represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)).

In the above-mentioned general formula (I), a is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.
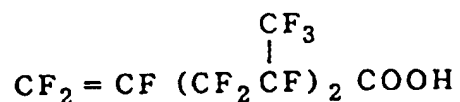
As detailed examples of the compound represented by the above-mentioned general formula (I), for example, $CF_2=CF-CF_2-COONH_4$, $CF_2=CF-CF_2-COOH$, $CF_2=CF-CF_2CF_2COOH$, $CF_2=CF-CF_2-COONa$, $CF_2=CF-CF_2-SO_3NH_4$, $CF_2=CF-CF_2-SO_3H$, $CF_2=CF-CF_2CF_2SO_3H$, $CF_2=CF-CF_2CF_2SO_3Na$, etc., are mentioned; however, $CF_2=CFCF_2COONH_4$ is preferable since an aqueous dispersion of the VdF copolymer with a high concentration and a small particle diameter is obtained.

In the above-mentioned general formula (II), X is preferably CF_3 in terms of stability of the compound, b is preferably an integer of 1-3 in terms of surface activity of the reactive emulsifier, Y is preferably COOM and SO_3M in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (II), for example,

$$CF_2=CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F-COOH \text{、} \quad CF_2=CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F-SO_3H \text{、}$$

$$CF_2=CF(CF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F)_2COONH_4 \text{、} \quad CF_2=CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}FSO_3NH_4 \text{、}$$

$$CF_2=CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F-COONa \text{、} \quad CF_2=CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F-SO_3Na \text{、}$$

$$CF_2=CF(CF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F)_2COOH$$

are mentioned; however,

$$CF_2 = CF \ (CF_2 \overset{\overset{\textstyle CF_3}{|}}{CF})_2 \ COOH$$

is preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (III), X is preferably F and CF_3 in terms of stability and weather resistance of the compound, c is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM and SO_3M in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (III), for example, $CF_2=CF-OCF_2CF_2CF_2COOH$, $CF_2=CF-OCF_2CF_2COONH_4$, $CF_2=CF-OCF_2COOH$, etc., are mentioned; however, $CF_2=CF-OCF_2CF_2CF_2COOH$ is preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (IV), X is preferably F and CF_3 in terms of stability and weather resistance of the compound, d is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM and SO_3M in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (IV), for example,

$CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COOH$, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COONH_4$, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2SO_3H$, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2SO_3NH_4$ or these ammonium salts, etc., are mentioned; however, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COOH$ and $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2SO_3H$ are preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (V), e is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM in terms of stability of the compound, and M is preferably Na and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (V), for example,

$$CH_2=CFCF_2OCF(CF_3)COONa \quad , \quad CH_2=CFCF_2OCFCF_2(CF_3)OCF(CF_3)COONa \quad ,$$

$$CH_2=CFCF_2O(CF(CF_3)CF_2O)_2CF(CF_3)COONa \quad ,$$

$$CH_2=CFCF_2OCF(CF_3)COONH_4 \quad , \quad CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COONH_4 \quad ,$$

$$CH_2=CFCF_2O(CF(CF_3)CF_2O)_2CF(CF_3)COONH_4$$

are mentioned; however, $CH_2=CFCF_2OCF(CF_3)COONH_4$ and $CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COONH_4$ are preferable since an aqueous

dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (VI), f is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (VI), for example,

$$CF_2{=}CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FCOOH\,,$$

$$CF_2{=}CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FCOONH_4\,,$$

$$CF_2{=}CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FSO_3H\,,$$

$$CF_2{=}CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FSO_3NH_4$$

are mentioned; however,

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FCOOH,$$

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FCOONH_4,$$

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FSO_3NH_4$$

is preferable since an aqueous dispersion of the VdF group copolymer with a small particle diameter is obtained.

In the present invention, the above-mentioned VdF seed polymer is a seed polymer of an ethylenically unsaturated monomer in which the particle of the above-mentioned VdF copolymer is a seed, and as said ethylenically unsaturated monomer, for example, a monomer having a functional group and a vinyl compound are mentioned. As the above-mentioned monomer having a functional group, for example, unsaturated carboxylic acid such as acrylic acid, methacrylic acid, maleic acid, and crotonic acid, an acrylic ester such as methyl acrylate, a methacrylic acid ester such as methyl methacrylate (MMA), an amide compound such as acrylamide, methacrylamide, N-methylacrylamide, N-methylolacrylamide, N-butoxymethylacrylamide, N-methylolmethacrylamide, N-methylmethacrylamide, and N-butoxymethylmethacrylamide, a monomer containing a hydroxyl group such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, and hydroxypropyl methacrylate, a monomer

containing an epoxy group such as glycidyl acrylate and glycidyl methacrylate, a monomer containing a silanol group such as γ-trimethoxysilane methacrylate and γ-triethoxysilane methacrylate, a monomer containing an aldehyde group such as acrolein, etc., are mentioned. As the above-mentioned vinyl compound, for example, styrene (St), acrylonitrile, etc., are mentioned; however, an acrylic ester and/or methacrylic ester are preferable in terms of compatibility with the VdF copolymer.

The VdF copolymer as part of the above-mentioned seed in the above-mentioned VdF seed polymer may also be a copolymer composed of said VdF, said reactive emulsifier, and another fluorinated monomer. As said other fluorinated monomer, for example, tetrafluoroethylene (TFE), trifluoroethylene (TrFE), chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), vinyl fluoride (VF), etc., are mentioned; however, TFE, HFP, and CTFE are preferable in terms of copolymerization reactivity of the VdF monomer.

As combinations of the VdF, said other fluorinated monomer, and said reactive emulsifier in the above-mentioned VdF copolymer, for example, a combination of any of VdF/TFE, VdF/TFE/HFP, VdF/TFE/CTFE, VdF/TFE/TrFE, VdF/CTFE, VdF/HFP, VdF/VFE/HFP/CTFE, etc., and any of $CF_2=CFCF_2COONH_4$, $CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COONH_4$, $CH_2=CFCF_2OCF(CF_3)COONH_4$, etc., is mentioned; however, a combination of VdF/TFE/CTFE and $CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COONH_4$ is preferable in terms of compatibility with an acrylic resin.

The copolymerization ratio of the above-mentioned VdF and the above-mentioned other fluorinated monomer in the above-mentioned VdF copolymer is 60/40-95/5 wt%, preferably

70/30-95/5 wt%. If said VdF is less than 60 wt%, the compatibility with the acrylic polymer, which is a characteristic of the VdF polymer, tends to decrease, and if it is more than 95 wt%, since the solubility of the seed particle into an acrylic ester and/or methacrylic acid ester is poor, the seed particle is not rapidly swollen to the monomer during seed polymerization. A cast film from the obtained emulsion has a poor transparency, and in preparing a film from the paint, gloss typically cannot be obtained.

The above-mentioned reactive emulsifier may be included at 0.001-0.1 mol% in relation to the combination of the above-mentioned monomer.

In the above-mentioned VdF seed polymer, the ethylenically unsaturated monomer is polymerized at 20-100 parts by weight in the presence of the VdF copolymer at 100 parts by weight as the above-mentioned seed part.

The average particle diameter of the above-mentioned VdF seed polymer is 250 nm or less, preferably 50-250 nm, and more preferably 100-160 nm. If the above-mentioned average particle diameter is less than 50 nm, the viscosity of the aqueous dispersion increases, and there is a tendency that the aqueous dispersion with high concentration cannot be obtained. If the diameter is more than 250 nm, the particles sediment and solidify during the storage of the aqueous dispersion, and the gloss tends to disappear when the film is prepared.

The concentration of the above-mentioned VdF seed polymer of the aqueous dispersion of the above-mentioned VdF seed polymer is 30-60%, preferably 35-55%, and more preferably 35-50%. If the above-mentioned concentration is less than 30%, viscosity adjustment is difficult in forming a paint, and drying of the

film tends to slow. If the concentration is more than 60%, the stability of the dispersed body system tends to decrease.

In the aqueous dispersion of the VdF seed polymer in the present invention, well-known fluorinated surfactants may also be included.

The above-mentioned well-known fluorinated surfactant is a mixture of one kind or two kinds or more of compounds, which include fluorine atoms in the structure and have the surface activity. For example, the acid represented by $X(CF_2)_nCOOH$ (X represents F or H, and n represents an integer of 6-20) and its alkali metal salt, ammonium salt, amine salt, or quaternary ammonium salt, the acid represented by $Y(CH_2CF_2)_mCOOH$ (Y represents F or C, and l and m represent an integer of 6-13) and its alkali metal salt, ammonium salt, amine salt, or quaternary ammonium salt, etc., are mentioned; however, the ammonium salt of perfluorooctanoic acid and the ammonium salt of perfluorononanoic acid are preferable in terms of weather resistance and water resistance.

The amount of said fluorinated surfactant used is 1.0% or less, preferably 0.5% or less, and more preferably 0.2% or less in relation to water. If the amount of said fluorinated surfactant used is more than 1.0%, when a film is formed from the aqueous dispersion, said fluorinated surfactant is precipitated in the film or the water absorption rate increases, so that the surfactant tends to whiten, which is not preferable.

In the aqueous dispersion of the VdF seed polymer in the present invention, a hydrophilic organic solvent can also be added.

The aqueous dispersion of the VdF seed polymer of the present invention can form an aqueous paint by mixing with

various kinds of additives. As the above-mentioned additives, for example, additives which are generally used in an aqueous paint, such as pigments, viscosity enhancers, dispersants, foaming agents, antifreezes, and film formation aids are mixed, so that a paint for building facades and a paint for civil structures can be formed.

Furthermore, the present invention is a manufacturing method for obtaining the aqueous dispersion of the VdF seed polymer by the emulsion polymerization of the ethylenically unsaturated monomer in the presence of VdF copolymer particles.

In obtaining the above-mentioned VdF copolymer, the VdF monomer and the reactive emulsifier may go through emulsion-polymerization, and the above-mentioned reactive emulsifier is a fluorinated compound having a polymerizable double bond and a hydrophilic group in the molecule and is a compound represented by at least one kind selected from the above-mentioned group comprised of the general formula (I):

$$CF_2=CF-(-CF_2-)_a-Y \qquad (I)$$

(where a represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (II):

$$CF_2=CF-(-CF_2CFX-)_b-Y \qquad (II)$$

(where X represents F or CF_3, b represents an integer of 1-5, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (III):

$$CF_2=CF-O-(-CFX-)_c-Y \qquad (III)$$

(where X represents F or CF_3, c represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (IV):

$$CF_2=CF-O-(-CF_2CFXO-)_d-CF_2CF_2-Y \qquad (IV)$$

(where X represents F or CF₃, d represents an integer of 1-10, Y represents SO₃M or COOM (M represents H, NH₄, or an alkali metal)), general formula (V):
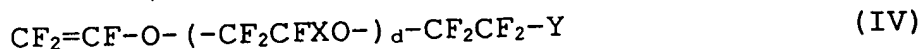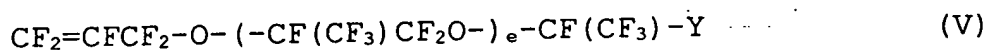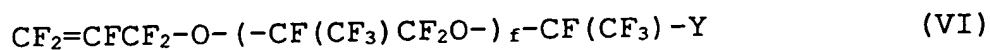
$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_e-CF(CF_3)-Y \qquad (V)$$

(where e represents an integer of 1-10, Y represents SO₃M or COOM (M represents H, NH₄, or an alkali metal)), and general formula (VI):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_f-CF(CF_3)-Y \qquad (VI)$$

(where f represents an integer of 1-10, Y represents SO₃M or COOM (M represents H, NH₄, or an alkali metal)).

In the above-mentioned general formula (I), a is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM in terms of stability of the compound, and M is preferably H and NH₄ in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (I), for example, CF₂=CF-CF₂-COONH₄, CF₂=CF-CF₂-COOH, CF₂=CF-CF₂CF₂COOH, CF₂=CF-CF₂-COONa, CF₂=CF-CF₂-SO₃NH₄, CF₂=CF-CF₂-SO₃H, CF₂=CF-CF₂CF₂SO₃H, CF₂=CF-CF₂CF₂SO₃Na, etc., are mentioned; however, CF₂=CFCF₂COONH₄ is preferable since an aqueous dispersion of the VdF copolymer with a high concentration and a small particle diameter is obtained.

In the above-mentioned general formula (II), X is preferably CF₃ in terms of stability of the compound, b is preferably an integer of 1-3 in terms of surface activity of the reactive emulsifier, Y is preferably COOM and SO₃M in terms of stability of the compound, and M is preferably H and NH₄ in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (II), for example,
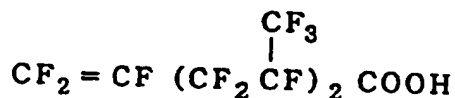
$$CF_2 = CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F-COOH \quad CF_2 = CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F-SO_3H$$

$$CF_2 = CF\,(CF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F)_2COONH_4 \quad CF_2 = CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}FSO_3NH_4$$

$$CF_2 = CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F-COONa \quad CF_2 = CFCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F-SO_3Na$$

$$CF_2 = CF\,(CF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F)_2\,COOH$$

are mentioned; however,

$$CF_2 = CF\,(CF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F)_2\,COOH$$

is preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (III), X is preferably F and CF_3 in terms of stability and weather resistance of the compound, c is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM and SO_3M in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (III), for example, $CF_2=CF-OCF_2CF_2CF_2COOH$, $CF_2=CF-OCF_2CF_2COONH_4$, $CF_2=CF-OCF_2COOH$, etc., are mentioned; however, $CF_2=CF-OCF_2CF_2CF_2COOH$ is preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (IV), X is preferably F and CF_3 in terms of stability and weather resistance of the compound, d is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM and SO_3M in terms of stability of the compound, and M is preferably H and NH_4 in terms of water resistance of the film.

As detailed examples of the compound represented by the above-mentioned general formula (IV), for example, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COOH$, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COONH_4$, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2SO_3H$, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2SO_3NH_4$ or these ammonium salts, etc., are mentioned; however, $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COOH$ and $CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2SO_3H$ are preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (V), e is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM in terms of stability of the compound, and M is preferably Na and NH_4 in terms of water resistance of the film.
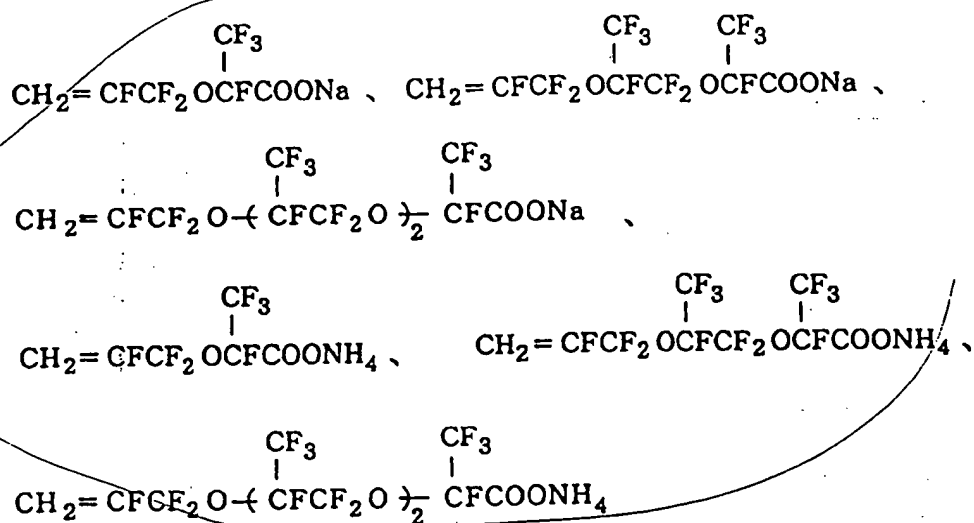
As detailed examples of the compound represented by the above-mentioned general formula (V), for example,

$$CH_2=CFCF_2O\underset{\underset{CF_3}{|}}{C}FCOONa \text{ 、} \quad CH_2=CFCF_2O\underset{\underset{CF_3}{|}}{C}FCF_2O\underset{\underset{CF_3}{|}}{C}FCOONa \text{ 、}$$

$$CH_2=CFCF_2O\!\!\left(\underset{\underset{CF_3}{|}}{C}FCF_2O\right)_{\!\!2}\underset{\underset{CF_3}{|}}{C}FCOONa \text{ 、}$$

$$CH_2=CFCF_2O\underset{\underset{CF_3}{|}}{C}FCOONH_4 \text{ 、} \quad CH_2=CFCF_2O\underset{\underset{CF_3}{|}}{C}FCF_2O\underset{\underset{CF_3}{|}}{C}FCOONH_4 \text{ 、}$$

$$CH_2=CFCF_2O\!\!\left(\underset{\underset{CF_3}{|}}{C}FCF_2O\right)_{\!\!2}\underset{\underset{CF_3}{|}}{C}FCOONH_4$$

are mentioned; however, $CH_2=CFCF_2OCF(CF_3)COONH_4$ and $CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COONH_4$ are preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

In the above-mentioned general formula (VI), f is preferably an integer of 1-5 in terms of surface activity of the reactive emulsifier, Y is preferably COOM in terms of stability of the compound, and M is preferably H and NH₄ in terms of water-resistance of the film.
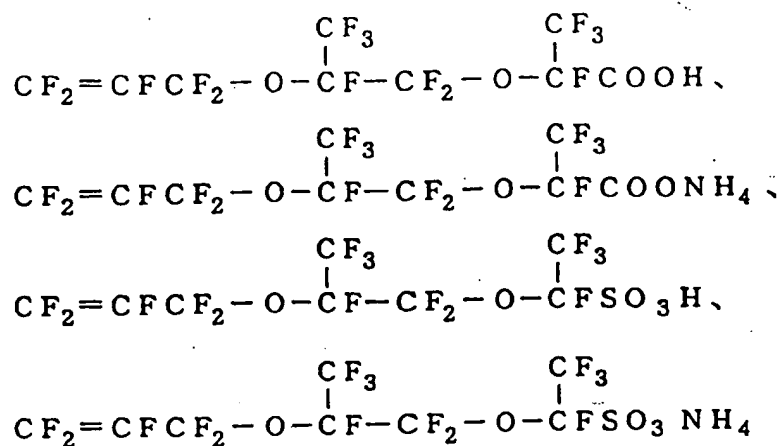
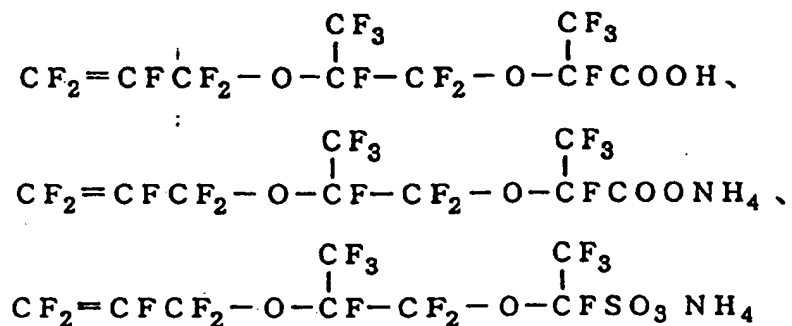As detailed examples of the compound represented by the above-mentioned general formula (VI), for example,

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FCOOH,$$

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FCOONH_4,$$

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FSO_3H,$$

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FSO_3NH_4$$

are mentioned; however,

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FCOOH,$$

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FCOONH_4,$$

$$CF_2=CFCF_2-O-\underset{\underset{CF_3}{|}}{C}F-CF_2-O-\underset{\underset{CF_3}{|}}{C}FSO_3NH_4$$

is preferable since an aqueous dispersion of the VdF copolymer with a small particle diameter is obtained.

When the above-mentioned VdF polymer and the above-mentioned reactive emulsifier go through emulsion-polymerized, other fluorinated monomers can also be used in addition to VdF. For example, tetrafluoroethylene (TFE), trifluoroethylene (TrFE), chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), vinyl fluoride (VF), etc., are mentioned; however, TFE, HFP, and CTFE are preferable in terms of copolymerization reactivity of the VdF monomer.

In the above-mentioned emulsion polymerization, well-known fluorinated surfactants can be used.

The above-mentioned well-known fluorinated surfactant is a mixture of one kind or two kinds or more of compounds which include fluorine atoms in the structure and have surface activity. For example, the acid represented by $X(CF_2)_nCOOH$ (X represents F or H, and n represents an integer of 6-20) and its alkali metal salt, ammonium salt, amine salt, or quaternary ammonium salt, the acid represented by $Y(CH_2CF_2)_mCOOH$ (Y represents F or C, and l and m represent an integer of 6-13) and its alkali metal salt, ammonium salt, amine salt, or quaternary ammonium salt, etc., are mentioned; however the ammonium salt of perfluorooctanoic acid and the ammonium salt of perfluorononanoic acid are preferable in terms of weather resistance and water resistance.

The amount of said fluorinated surfactant used is 1.0% or less, preferably 0.5% or less, and more preferably 0.2% or less in relation to water. If the amount of said fluorinated surfactant used is more than 1.0%, when a film is formed from the aqueous dispersion, said fluorinated surfactant is precipitated in the film or the water absorption rate increases, so that the surfactant tends to whiten, which is not preferable.

In manufacturing the aqueous dispersion of the above-mentioned VdF seed polymer, water is charged as a polymerization solvent into a reactor, and the above-mentioned reactive emulsifier is charged at 0.00001-10%, preferably 0.0001-1.0%, and more preferably 0.001-0.5% in relation to said polymerization solvent. Then, the dissolved air is removed by repeating nitrogen pressurization and degassing.

Here, if the amount of said reactive emulsifier charged is less than 0.00001%, large particles with insufficient sedimentation stability tend to form. If the amount is more than 10%, the shape of the particles is not spherical, and when the film formability tends to decrease when drying the aqueous dispersion.

Next, the above-mentioned VdF monomer or a mixed monomer with another fluorinated monomer is supplied while pressurizing up to a pressure of 1.0-50 kgf/cm^2.

At that time, the mixture ratio of the above-mentioned other fluorinated monomer may be 0-30 wt%.

Next, as a polymerization initiator, for example, a persulfate such as ammonium persulfate, hydrogen peroxide, diisopropyl peroxydicarbonate, azobisisobutylonitrile, etc., is charged at 0.0001-0.5%, preferably 0.001-0.1% in relation to water. If the amount of said polymerization initiator charged is less than 0.0001%, the polymerization rate which is of practical use, tends to decrease extremely. If the amount is more than 0.5%, controlling the reaction heat tends to be difficult.

Furthermore, the above-mentioned VdF monomer or the above-mentioned mixed monomer is continuously supplied so that the pressure in the reactor can be constant in a range of 1-50 kgf/cm^2, preferably 5-40 kgf/cm^2. If the above-mentioned

pressure is less than 1 kgf/cm^2, the polymerization rate which is of practical use cannot be obtained, and if the pressure is more than 50 kgf/cm^2, controlling the reaction heat tends to be difficult.

In the above-mentioned state, polymerization is carried out for 5-100 h.

Then, the interior of the above-mentioned reactor returns to normal temperature and normal pressure, and polymerization is completed, so that the aqueous dispersion of the VdF copolymer is obtained.

Next, in the aqueous dispersion of the above-mentioned VdF copolymer, the above-mentioned ethylenically unsaturated monomer at 20-100 parts by weight, preferably 30-100 parts by weight, and more preferably 40-100 parts by weight is added to the VdF copolymer at 100 parts by weight.

Here, if the amount of said ethylenically unsaturated monomer is less than 20 parts by weight, the transparency and gloss during film formation tend to decrease.

Furthermore, right after this, a persulfate such as ammonium persulfate, etc., is added at 0.05-2.0 parts by weight as a polymerization initiator to the above-mentioned ethylenically unsaturated monomer at 100 parts by weight, and polymerization is started. After polymerization is carried out at a temperature of 20-90°C for 0.5-6 h, the pH is adjusted, and the aqueous dispersion of the VdF seed polymer is obtained by filtering with a wire net.

The average particle diameter of the VdF seed polymer of the aqueous dispersion of the VdF seed polymer obtained by the above-mentioned manufacturing method can be controlled to 250 nm or

less, and said average particle diameter can be controlled by the amount of said reactive emulsifier charged.

Also, the concentration of the VdF seed polymer of the aqueous dispersion of the VdF seed polymer obtained by the above-mentioned manufacturing method can be controlled to 30-60%, and said concentration can be controlled by blowing the VdF monomer or mixed monomer when a prescribed amount of said VdF monomer or said mixed monomer is continuously supplied to the reactor, stirring is stopped, and the reaction is completed.

Next, the present invention is explained in further detail based on the application examples; however, the present invention is not limited to them.

Also, the number and the structural formula of the reactive emulsifier used in the following application examples and comparative examples are shown in Table I.

Table I

反応性乳化剤番号	反 応 性 乳 化 剤 の 構 造 式
1	$CF_2=CFCF_2-COOH$
2	$CF_2=CF-O-CF_2CF_2CF_2-COOH$
3	$CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-COOH$
4	$CF_2=CF-O-CF_2CF(CF_3)-OCF_2CF_2-SO_3H$
5	$CH_2=CFCF_2-O-CF(CF_3)CF_2O-CF(CF_3)-COOH$
6	$CH_2=CFCF_2-O-CF(CF_3)-COOH$
7	$CF_2=CFCF_2-O-CF(CF_3)CF_2-O-CF(CF_3)-COOH$

Key: 1   Reactive Emulsifier No.
     2   Structural formula of the reactive emulsifier

Application Example 1

500 mL deionized water and 5.0 g reactive emulsifier (No. 1) shown in Table I were charged into a pressure-resistant reactor with a stirrer having an interior capacity of 1 L, and the dissolved air was removed by repeating nitrogen pressurization and degassing. Then, a mixed monomer of VdF (80 mol%) and TFE (20 mol%) was pressurized until the interior pressure of said container was 10 kgf/cm^2 at 60°C. Next, 0.2 g ammonium persulfate was charged, and the above-mentioned monomer was continuously supplied so that the interior pressure of the above-mentioned container was constant at 10 kgf/cm^2. Polymerization was carried out for 20 h, and the interior of said container was returned to normal temperature and normal pressure. After polymerization was completed, an aqueous dispersion of a VdF copolymer of the present invention was obtained, and the following tests were carried out.

The tests were carried out as follows.

Solid fraction concentration: The above-mentioned aqueous dispersion was dried at 150°C for 1 h in a vacuum dryer, and the weight after drying is indicated by percentage of the weight of the aqueous dispersion before drying.

Average particle diameter: It was measured by a laser-beam scattering particle diameter measuring apparatus (made by Otsuka Denshi K.K., trade name: ELS-3000).

Particle size distribution: It was measured by the laser-beam scattering particle diameter measuring apparatus (made by

Otsuka Denshi K.K., trade name: ELS-3000), and the ratio (dw/dn) of the weight-average particle diameter dw to the number-average particle diameter dn is designated as the particle size distribution.

Sedimentation stability: The above-mentioned aqueous dispersion was held at 25°C for 60 days and evaluated as follows.

When there was no change in the dispersed state by observation with the naked eye, it was designated o. Although the particles were sedimented and the phases were separated, when redispersion was enabled by vibrating, it was designated as Δ. Furthermore, when the particles were sedimented, the phases were separated, redispersion did not occur even by vibrating, it was designated as x.

The results are shown in Table II.

Application Examples 2-13

According to a method similar to that of Application Example 1 except for adopting the polymerization conditions shown in Table II in Application Example 1, an aqueous dispersion of a VdF copolymer of the present invention was obtained, and tests similar to those of Application Example 1 were carried out. The results are shown in Table II.

Comparative Examples 1-6

According to a method similar to that of Application Example 1 except for adopting the polymerization conditions shown in Table II in Application Example 1, an aqueous dispersion of a VdF copolymer or an aqueous dispersion of a tetrafluoroethylene-

propylene copolymer was obtained, and tests similar to those of
Application Example 1 were carried out. The results are shown in
Table II.

Table II

			① 実 施 例													② 比 較 例					
⑤			1	2	3	4	5	6	7	8	9	10	11	12	13	1	2	3	4	5	6
重合条件 ③	供給モノマー（モル％）	VdF[1]	80	80	80	80	100	80	75	72	75	75	80	75	75	80	75	72	75	40	-
		TFE[1]	20	20	20	20	-	20	15	20	15	15	20	15	15	20	15	20	15	60	50
		CTFE[1]	-	-	-	-	-	-	10	-	10	10	-	10	10	-	10	-	10	-	-
		HFP[1]	-	-	-	-	-	-	-	8	-	-	-	-	-	-	-	8	-	-	-
		P[1]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	50
	反応性乳化剤番号		1	2	3	4	5	5	5	5	5	5	7	6	5	-	-	-	-	5	5
	水に対する添加量（重量％） ⑥		1.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.5	0.01	0.1	0.5	0.5	-	-	-	-	1.0	1.0
	パーフルオロオクタン酸アンモニウム塩の水に対する添加量（重量％） ⑦		-	-	-	-	-	-	-	-	-	-	-	-	0.1	1.0	0.5	0.1	2.0	-	-
	重合圧力（kgf/cm²G） ⑧		10	10	10	10	20	10	8	8	8	8	10	8	8	10	8	8	8	8	10
	重合時間（hr） ⑨		20	27	25	23	36	24	25	21	30	50	26	25	26	20	23	21	16	13	68
試験 ④	固形分濃度（重量％） ⑩⑪		31.0	30.5	31.2	30.3	30.2	30.6	37.4	34.3	39.9	35.0	31.6	32.0	41.9	24.6	34.6	32.0	38.8	21.1	30.1
	平均粒子径（nm）		178.1	162.3	173.1	154.7	131.4	120.0	116.2	105.8	100.4	156.4	131.3	49.2	104.3	269.2	221.6	234.5	68.5	216.0	231.6
	粒度分布（dw/dn） ⑫		1.27	1.54	1.48	1.55	1.38	1.38	1.56	1.43	1.45	1.59	1.27	1.39	1.02	1.08	1.05	1.03	1.12	2.04	1.51
	沈降安定性 ⑬		○	○	○	○	○	○	○	○	○	○	○	○	○	×	×	×	△	×	△

1) VdF: Vinylidene fluoride, TFE: Tetrafluoroethylene, CTFE:
    Chlorofluoroethylene, HFP: Hexafluoropropylene, P:
    Propylene

Key: 1   Application Example
     2   Comparative Example
     3   Polymerization conditions
     4   Test
     5   Supplied monomer (mol%)
     6   Reactive emulsifier No.
          Amount added to water (wt%)

7	Amount of ammonium perfluorooctanoate to water (wt%)
8	Polymerization pressure (kgf/cm^2)
9	Polymerization time (h)
10	Solid fraction concentration (wt%)
11	Average particle diameter (nm)
12	Particle size distribution (dw/dn)
13	Sedimentation stability

Application Example 14

70 g of an aqueous dispersion of the VdF copolymer obtained in Application Example 7 was charged into a four-necked flask with an interior capacity of 200 mL and equipped with a stirring blade, cooling tube, and thermometer, and 0.5% alkali salt of an alkylallyl sulfosuccinate (made by Sanyo Chemical Industries, Ltd., trade name: Ereminol[transliteration] JS2) as a polymerizable emulsifier to a resin solid fraction was added to it to secure the stability of the seed particles during seed polymerization. It was heated in a water bath while stirring, and when the temperature of the interior of said flask reached 80°C, an emulsion in which 11.2 g methyl methacrylate (hereinafter, abbreviated to MMA) monomer and 1.5 g polyoxyethylene methacrylic acid ester (made by Nippon Oil and Fats Co., Ltd., trade name: PME400, added molar number of ethylene oxide of 9) were emulsified in a 0.5% aqueous solution of the alkali salt of said alkylallyl sulfosuccinate, was added dropwise for 1 h. Right after this, 1 mL of a 2% aqueous solution of ammonium persulfate was added, and polymerization was started. 3 h after the polymerization start, the temperature of the interior of the above-mentioned flask was raised to 85°C, held for 1 h, and

cooled, and the pH was adjusted to 7 with ammonia water. A blue-
white aqueous dispersion of a VdF seed polymer of the present
invention was obtained by filtering with a 300-mesh wire net, and
the following tests were carried out.

The tests were carried out as follows.

(1) Test of the aqueous dispersion of the VdF seed polymer

Solid fraction concentration and average particle diameter:
They were carried out by the same methods as those of Application
Example 1.

Viscosity: It was measured at 25°C with a B type viscometer.

Minimum film formation temperature (MFT): When a continuous
film was formed, the minimum temperature was measured by a heat-
gradient tester (made by Rikagaku Kogyo K.K.).

(2) Test of the film obtained by forming from the aqueous
  dispersion of the above-mentioned VdF seed polymer

Transparency: The aqueous dispersion was placed in a petri
dish with a diameter of 10 cm so that the thickness of the dried
film was 200 µm, and it was dried at 80°C for 24 h. The light
transmittance of the film at a wavelength of 800 nm was measured
and evaluated as follows.

When the film was transparent (a transmittance of more than
90%), it was designated as o, and when the film was
semitransparent (a transmittance of 60-90%), it was designated as
Δ. When the film was whitened (a transmittance of less than
60%), it was designated as x.

Water resistance: The above-mentioned film was cut at

2 cm x 4 cm, immersed for one week in 50°C warm water, and the increase ratio of the weight calculated from the following equation was designated as the water absorption rate.

Water absorption rate (%) = ((weight after immersion - initial weight) / (initial weight)) x 100

Also, after redrying, the reduction ratio of the weight calculated from the following equation was designated as the elution fraction.

Elution fraction (%) = ((initial weight - weight after redrying)/(initial weight)) x 100

(3) Test of the film obtained from the aqueous dispersion of the above-mentioned VdF seed polymer

Titanium oxide (made by Ishihara Sangyo Kaisha, Ltd., trade name: CR90) as a filler at 50 parts by weight, Discoat[transliteration] H-14 (made by Nippon Emulsifier K.K.) as a dispersant at 2 parts by weight, ethylene glycol as an antifreeze at 1 part by weight, FS Antifoam 013B (made by Nippon Emulsifier K.K.) as an antifoaming agent at 0.5 part by weight, SN thickener A-818 (made by Sannopuko K.K.) as a viscosity enhancer at 0.5 part by weight, and Texanol[transliteration] CS12 (made by Chisso Corporation) as a film formation aid at 10 parts by weight were added to the resin solid fraction at 100 parts by weight of the aqueous dispersion obtained in Application Example 14 and sufficiently mixed by a dispersing stirrer, so that a paint was manufactured. Then, the following tests were carried out.

Gloss: The obtained paint was extended at a film thickness of 20 μm on a glass plate by an applicator and dried at room

temperature for one week, and the gloss with a reflection angle of 60° was measured by a glossimeter.

Weather resistance: The obtained paint was spread on a spray plate, which was sealed with an aqueous epoxy resin sealer EM-0150 (made by Sanyo Chemical Industries, Ltd.), with an air spray gun so that the thickness of the film after drying was 100 µm. The spray plate was dried at room temperature for 24 h and dried at 80°C for 2 h. After the spray plate was passed for 1000 h through a stimulative weather-resistant tester (SUV), the gloss retention rate was measured and evaluated as follows.

When the gloss retention rate was more than 80%, it was designated as o, and when the gloss retention rate was 60-80%, it was designated as Δ. When the gloss retention rate was less than 60%, it was designated as x.

Alkali resistance: The spray plate obtained by a method similar to that of the weather resistance test was immersed at 50°C for one week into 3% aqueous NaOH solution, and coloring and swelling of the film were judged with the naked eye.

Acid resistance: The spray plate obtained by a method similar to that of the weather resistance test was immersed at 50°C for one week in a 1% acidic solution, and coloring and swelling of the film were judged with the naked eye.

The results are shown in Table III.

Application Examples 15-17

According to a method similar to that of Application Example 14 except for adopting the seed polymerization conditions shown in Table III in Application Example 14, an aqueous dispersion of a VdF seed polymer of the present invention was obtained, and

tests similar to those of Application Example 14 were carried out. The results are shown in Table III.

Comparative Examples 7-8

According to a method similar to that of Application Example 14 except for adopting the seed polymerization conditions shown in Table III in Application Example 14, an aqueous dispersion of a VdF seed polymer was obtained, and tests similar to those of Application Example 14 were carried out. The results are shown in Table III.

Table III

		実　施　例				比　較　例	
		14	15	16	17	7	8
シード重合の条件	使用した水性分散液の種類 使用量（g）	実施例7でえられた水性分散液 70	実施例9でえられた水性分散液 70	実施例13でえられた水性分散液 70	実施例12でえられた水性分散液 70	比較例2でえられた水性分散液 70	比較例4でえられた水性分散液 70
	MMA（g）	11.2	12.0	12.6	9.6	10.4	11.6
	PME400（g）	1.5	1.6	1.7	1.3	1.4	1.6
試験	固形分濃度（重量％）	42.8	45.9	47.8	38.6	41.1	44.2
	粘度（CP）	56	100	110	68	10	83
	平均粒子径（nm）	136.3	120.5	126.1	60.2	277.9	87.3
	最低造膜温度（℃）	43	42	39	36	59	47
	透明性	○	○	○	○	△	×
	吸水率（％）	1.8	2.3	3.2	1.5	13.7	24.6
	溶出分率（％）	0.5	0.3	0.3	0.2	2.6	8.3
	光沢（60°G）	75	78	76	78	56	32
	耐候性	○	○	○	○	○	△
	耐酸性	異常なし	異常なし	異常なし	異常なし	異常なし	異常なし
	耐アルカリ性	異常なし	異常なし	異常なし	異常なし	わずかにフクレ	フクレ、着色

Key: 1   Application Example
2   Comparative Example
3   Seed polymerization conditions
4   Test
5   Kind of aqueous dispersion used
     Amount used (g)
6   Aqueous dispersion obtained in Application Example
7   Aqueous dispersion obtained in Comparative Example
8   Solid fraction concentration (wt%)
9   Viscosity (CP)
10'   Average particle diameter (nm)
11   Minimum film formation temperature (°C)
12   Transparency
13   Water absorption rate (%)
14   Elution fraction (%)
15   Gloss (60° G)
16   Weather resistance
17   Acid resistance
18   Alkali resistance
19   No abnormality
20   Slight swelling
21   Swelling, colored

As seen from the results of Table III, in case only the ammonium perfluorooctanonate without reactivity is used as an emulsifier, the particle diameter is increased by the use of a small amount, and a high-gloss film cannot be obtained. In case a large amount is used, the transparency of the formed film is lowered, and the gloss of the film is not exhibited. Also, the decrease of the water resistance and the weather resistance of the film is recognized.

On the other hand, in the present invention, in case the reactive emulsifier is used, not only are all of the above-

mentioned properties met, but an aqueous dispersion film with a low MFT is obtained even in a resin with the same composition.

Industrial application field

In the aqueous dispersion of the VdF copolymer of the present invention, the average particle diameter of the VdF copolymer of said dispersion is as small as 200 nm or less, and the solid fraction concentration of said dispersion is as high as 30-60%. The sedimentation stability is also excellent.

Also, the method for manufacturing the aqueous dispersion of the VdF copolymer of the present invention can provide a method for manufacturing said dispersion with an average particle diameter of the VdF copolymer as small as 200 nm or less and a solid fraction concentration of said dispersion as high as 30-60% by copolymerizing a reactive emulsifier and a VdF monomer.

Furthermore, in the aqueous dispersion of the VdF seed polymer of the present invention, the average particle diameter of the VdF seed polymer of said dispersion is as small as 250 nm or less, and the solid fraction concentration of said dispersion is as high as 30-60%. The sedimentation stability is also excellent. The film obtained from said dispersion has excellent transparency and favorable water resistance, and the aqueous paint obtained from said dispersion has high gloss and excellent weather resistance, acid resistance, and alkali resistance.

Furthermore, the method for manufacturing the aqueous dispersion of the VdF seed polymer of the present invention can provide a method for manufacturing the aqueous dispersion of the VdF seed polymer obtained by the seed polymerization an ethylenically unsaturated monomer in the presence of VdF copolymer particles

obtained by copolymerizing a VdF monomer and a reactive emulsifier and can provide a method for manufacturing said dispersion with an average particle diameter of the VdF seed polymer of said dispersion as small as 250 nm or less, a solid fraction concentration of said dispersion as high as 30-60%, and excellent sedimentation stability.

Claims

1. An aqueous dispersion of a vinylidene fluoride copolymer characterized by the fact that in an aqueous dispersion of a vinylidene fluoride copolymer of a vinylidene fluoride monomer and at least one reactive emulsifier selected from a group comprised of general formula (I):
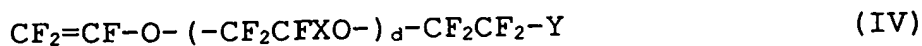
$$CF_2=CF-(-CF_2-)_a-Y \qquad (I)$$

(where a represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (II):
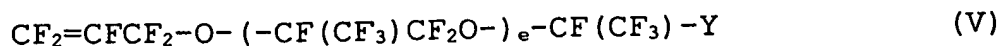
$$CF_2=CF-(-CF_2CFX-)_b-Y \qquad (II)$$

(where X represents F or CF_3, b represents an integer of 1-5, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (III):
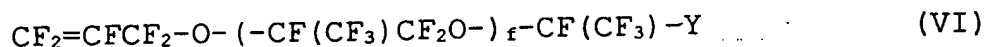
$$CF_2=CF-O-(-CFX-)_c-Y \qquad (III)$$

(where X represents F or CF_3, c represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (IV):

$$CF_2=CF-O-(-CF_2CFXO-)_d-CF_2CF_2-Y \qquad (IV)$$

(where X represents F or CF_3, b represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (V):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_e-CF(CF_3)-Y \qquad (V)$$

(where e represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), and general formula (VI):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_f-CF(CF_3)-Y \qquad (VI)$$

(where f represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), the solid fraction concentration is 30-60 wt% and that the average particle diameter of said copolymer is 200 nm or less.

2. A method for manufacturing the aqueous dispersion of the vinylidene fluoride copolymer characterized by the fact that in manufacturing the aqueous dispersion of the vinylidene fluoride copolymer by emulsion polymerization a vinylidene fluoride monomer and a reactive emulsifier, as said reaction emulsifier, at least one kind selected from a group comprised of general formula (I):
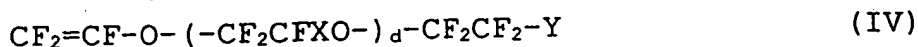
$$CF_2=CF-(-CF_2-)_a-Y \qquad (I)$$

(where a represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (II):

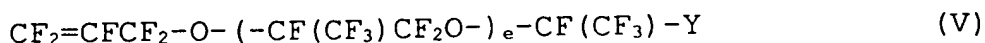$$CF_2=CF-(-CF_2CFX-)_b-Y \qquad (II)$$

(where X represents F or CF_3, b represents an integer of 1-5, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (III):

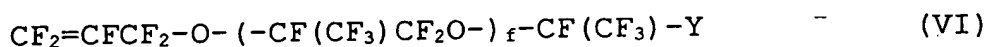$$CF_2=CF-O-(-CFX-)_c-Y \qquad (III)$$

(where X represents F or CF_3, c represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (IV):

$$CF_2=CF-O-(-CF_2CFXO-)_d-CF_2CF_2-Y \qquad (IV)$$

(where X represents F or CF_3, d represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (V):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_e-CF(CF_3)-Y \qquad \text{(V)}$$
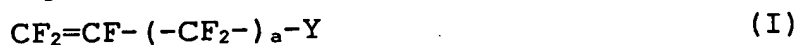
(where e represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), and general formula (VI):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_f-CF(CF_3)-Y \qquad \text{(VI)}$$

(where f represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)) is used at 0.00001-10 wt%; that the solid fraction concentration is set to 30-60 wt%; that the average particle diameter of said copolymer is set to 200 nm or less.

3. An aqueous dispersion of a vinylidene fluoride seed polymer characterized by the fact that in an aqueous dispersion of a vinylidene fluoride seed polymer obtained by the emulsion polymerization of an ethylenically unsaturated monomer in the presence of vinylidene fluoride copolymer particles, said vinylidene fluoride copolymer is a copolymer of a vinylidene fluoride monomer and at least one reactive emulsifier selected from a group comprised of general formula (I):
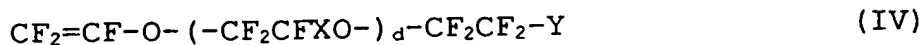
$$CF_2=CF-(-CF_2-)_a-Y \qquad \text{(I)}$$

(where a represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (II):

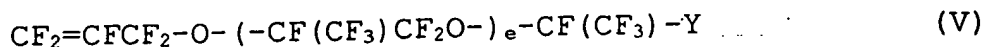$$CF_2=CF-(-CF_2CFX-)_b-Y \qquad \text{(II)}$$

(where X represents F or CF_3, b represents an integer of 1-5, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (III):

$$CF_2=CF-O-(-CFX-)_c-Y \qquad \text{(III)}$$

(where X represents F or CF_3, c represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (IV):

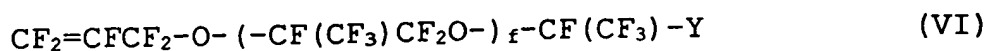$$CF_2=CF-O-(-CF_2CFXO-)_d-CF_2CF_2-Y \qquad \text{(IV)}$$

(where X represents F or CF$_3$, d represents an integer of 1-10, Y represents SO$_3$M or COOM (M represents H, NH$_4$, or an alkali metal)), general formula (V):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_e-CF(CF_3)-Y \qquad (V)$$

(where e represents an integer of 1-10, Y represents SO$_3$M or COOM (M represents H, NH$_4$, or an alkali metal)), and general formula (VI):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_f-CF(CF_3)-Y \qquad (VI)$$

(where f represents an integer of 1-10, Y represents SO$_3$M or COOM (M represents H, NH$_4$, or an alkali metal)); that the solid fraction concentration of the aqueous dispersion of said seed polymer is 30-60 wt%; that the average particle diameter of said seed copolymer is 250 nm or less.

4. A method for manufacturing the aqueous dispersion of the vinylidene fluoride seed polymer characterized by the fact that in manufacturing the aqueous dispersion of the vinylidene fluoride seed polymer by the emulsion polymerization of an ethylenically unsaturated monomer in the presence of vinylidene fluoride copolymer particles, said vinylidene fluoride copolymer is manufactured by the emulsion polymerization of vinylidene fluoride monomer and water and 0.00001-10 wt% of at least one reactive emulsifier selected from a group comprised of general formula (I):
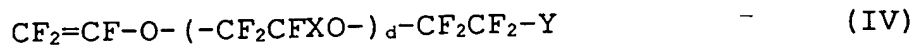
$$CF_2=CF-(-CF_2-)_a-Y \qquad (I)$$

(where a represents an integer of 1-10, Y represents SO$_3$M or COOM (M represents H, NH$_4$, or an alkali metal)), general formula (II):
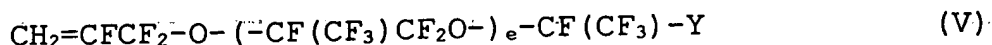
$$CF_2=CF-(-CF_2CFX-)_b-Y \qquad (II)$$

(where X represents F or CF$_3$, b represents an integer of 1-5, Y represents SO$_3$M or COOM (M represents H, NH$_4$, or an alkali metal)), general formula (III):

$$CF_2=CF-O-(-CFX-)_c-Y \qquad (III)$$

(where X represents F or CF_3, c represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (IV):
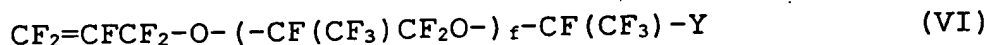
$$CF_2=CF-O-(-CF_2CFXO-)_d-CF_2CF_2-Y \qquad (IV)$$

(where X represents F or CF_3, d represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), general formula (V):

$$CH_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_e-CF(CF_3)-Y \qquad (V)$$

(where e represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)), and general formula (VI):

$$CF_2=CFCF_2-O-(-CF(CF_3)CF_2O-)_f-CF(CF_3)-Y \qquad (VI)$$

(where f represents an integer of 1-10, Y represents SO_3M or COOM (M represents H, NH_4, or an alkali metal)); that the solid fraction concentration of the aqueous dispersion of said seed polymer is set to 30-60 wt%; that the average particle diameter of said seed copolymer is set to 250 nm or less.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP95/01679

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^6 C08L27/16, C09D127/16, C08L51/06, C09D151/06, C08F214/22, C08F216/14, C08F259/09

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) Int. Cl^6 C08L27/00-27/24, C09D127/00-127/24, C08L51/00-51/10, C09D151/00-151/10, C08F214/18-214/28, C08F216/12-216/20, C08F259/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926 – 1995
Kokai Jitsuyo Shinan Koho	1971 – 1995
Toroku Jitsuyo Shinan Koho	1994 – 1995

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI/L

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 2-16326, B2 (The Dow Chemical Co.), April 16, 1990 (16. 04. 90), Claim & US, 4330654, A & EP, 41735, B1 & DE, 3169130, B2	1 – 4
A	JP, 4-325509, A (Japan Synthetic Rubber Co., Ltd.), November 13, 1992 (13. 11. 92), Claim (Family: none)	1 – 4
A	JP, 2-132101, A (Kao Corp.), May 21, 1990 (21. 05. 90), Claim (Family: none)	1 – 4
A	JP, 2-48579, B2 (Asahi Glass Co., Ltd.), October 25, 1990 (25. 10. 90), Claim & EP, 50447, B1 & DE, 3172534, B2 & US, 4385150, A	1 – 4

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
November 10, 1995 (10. 11. 95)	November 28, 1995 (28. 11. 95)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)